Secondary organic aerosol
2. Thermodynamic model for gas/particle partitioning of molecular constituents

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[1] A model that predicts secondary organic aerosol (SOA) formation based on the thermodynamic equilibrium partitioning of secondary organic oxidation products has been developed for implementation into atmospheric models. Hydrophobic secondary products are assumed to partition to an absorbing organic aerosol consisting of primary organic aerosol (POA) and other secondary hydrophobic organics according to an equilibrium partitioning coefficient calculated iteratively for each secondary compound present. The hydrophobic module is evaluated by studying the partitioning of octadecanoic acid to surrogate POA species. As expected, the amount of octadecanoic acid predicted to be present in the aerosol phase increases as the total amount of absorbing material increases or as the total amount of acid present increases. Hydrophilic secondary compounds partition to an aqueous phase via Henry's law; the fraction of each compound's mass that partitions is determined by its Henry's law constant and its acid dissociation constant(s). The available liquid water content (LWC) of the aerosol is determined iteratively between an inorganic aerosol module and the hydrophilic module, which is evaluated by studying the partitioning of glyoxalic and malic acids. While glyoxalic acid tends to remain in the gas phase, malic acid partitions strongly to the aqueous phase, with ions being the dominant form in the aqueous phase. As expected, an increase in relative humidity increases the amount of water associated with the organics (ΔLWC), and a lower aerosol pH favors molecular solutes over ionized forms. Increasing pH results in higher effective Henry's law constants for the acids, yielding higher organic aerosol concentrations. Results also indicate that increasing ΔLWC induces additional partitioning of inorganics to the aqueous phase. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS:* secondary organic aerosol, biogenic aerosol, photooxidation, urban air quality

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1. Introduction

[2] Organic aerosol (OA) is a significant constituent of particulate matter (PM) [*Stevens et al.*, 1984; *White and Macias*, 1989; *Penner*, 1995; *United States Environmental Protection Agency*, 1996; *Murphy et al.*, 1998]. For example, in major urban areas such as Philadelphia, Los Angeles, and Chicago, OA has been observed to make up as much as one half of the mass of the measured PM [*United States Environmental Protection Agency*, 1996]. OA can be both primary (POA, emitted as aerosol) and secondary (SOA, formed in situ in the atmosphere as condensable vapors). Sources of POA include, among others, combustion processes [*Schauer*, 1998; *Schauer et al.*, 1999a, 1999b]. SOA is formed as a result of the oxidation of both anthropogenic and biogenic organic species [*Odum et al.*, 1996, 1997; *Hoffmann et al.*, 1997; *Griffin et al.*, 1999]. Oxidation of these species leads to the formation of products that tend to contain a high degree of functionality, including hydroxy, carbonyl, carboxy, nitrooxy, and nitro groups [see, e.g., *Atkinson*, 1994, 1997, and references therein; *Smith et al.*, 1999; *Yu et al.*, 1999]. Those products with sufficiently low vapor pressures will partition between the gas and aerosol phases, forming SOA and contributing to the overall PM burden. Some of these products may also partition to the aerosol aqueous phase [*Saxena and Hildemann*, 1996].

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[3] Inorganic aerosol thermodynamic equilibrium models are now incorporated in atmospheric aerosol models [see, e.g., *Jacobson*, 1997; *Ansari and Pandis*, 1999; *Zhang et al.*, 2000, and references therein]. Because of the large number of organic compounds in the atmosphere and because methods to predict their thermodynamic properties in complex organic-water mixtures pose significant theoretical challenges, current gas-aerosol thermodynamic models for organic atmospheric species do not include the same level of detail as those for inorganic species. Experimentally based gas-particle distribution factors for complex mixtures generated by the photooxidation of aromatic and biogenic hydrocarbons are available [*Odum et al.*, 1996, 1997; *Hoffmann et al.*, 1997; *Griffin et al.*, 1999]. The goal is, however, a fundamentally based thermodynamic model that predicts the phase partitioning of individual organic compounds between the gas phase and condensed-phase organic-inorganic-water mixtures. Such a model would afford a first-principles prediction of the amount of OA formed from secondary species in the atmosphere.

[4] This paper presents a module that predicts the equilibrium partitioning of SOA and that is designed for use in a three-dimensional atmospheric model. Concentrations of secondary organic oxidation products predicted by a gas-phase chemical mechanism (part 1, by *Griffin et al.* [2002]) are partitioned between the gas and aerosol phases by this module. The equilibrium partitioning module will be incorporated in a comprehensive gas-and particle-phase air quality model for simulations of a 1993 smog episode in the South Coast Air Basin (SoCAB) of California (part 3).

2. Review of Previous Techniques to Model SOA

[5] Atmospheric models have been developed that include some treatment of SOA formation [*Jacobson*, 1997; *Lurmann et al.*, 1997; *Meng et al.*, 1998; *Sun and Wexler*, 1998; *Pai et al.*, 2000]. The current approaches used to model SOA formation, however, fail to provide a fundamental treatment of the gas/partitioning processes over a wide range of conditions. Detailed gas-phase mechanisms for SOA formation that have been developed have been limited to chemical systems studied in smog chamber experiments [*Barthelmie and Pryor*, 1999; *Kamens et al.*, 1999].

2.1. Fractional Aerosol Coefficient

[6] The simplest method that attempts to account for the conversion of a given parent species from the gas phase to oxidation products in the particle phase is based on the fractional aerosol coefficient (FAC). The FAC is defined as the ratio of the SOA formed from a parent organic to the initial amount of that parent species present in a chamber experiment [*Grosjean*, 1992]. The FAC method does not take into account the time needed to form SOA in the atmosphere or the concentrations of available oxidants. Therefore, the amount of the parent species that reacts is not treated explicitly. Because the technique considers no kinetics, SOA can be treated as if it were emitted. As a result, the FAC applies only to conditions for which it was derived; FAC values do not take into account temperature, relative humidity, or initial particle concentrations. Thus, FAC values cannot provide realistic SOA estimates for air quality modeling.

2.2. Fixed Aerosol Yield

[7] A second method for estimating SOA formation based on the concentrations of precursors is to assume a fixed SOA yield for a given parent organic. In contrast to the FAC, this approach takes into account the time needed to form SOA, and the yield is defined as the amount of organic aerosol mass that forms per amount of the parent organic mass that reacts [*Pandis et al.*, 1992]. Thus, this method takes the reactivity of the parent organic and the availability of oxidants into account. The limitations associated with estimating SOA formation using this method are that there is no dependence of the yield on the existing particle phase, temperature, or relative humidity. Given that yield depends on these variables, it is difficult to determine which experimentally determined yield is the most appropriate to use when modeling conditions vary temporally and spatially and deviate significantly from smog chamber conditions.

2.3. Saturation of Oxidation Products

[8] It has been assumed in earlier work that a product formed from the oxidation of a parent organic condenses into the particle phase only when its saturation vapor pressure has been reached [*Pandis et al.*, 1992]. The amount of SOA formed is thus defined as the difference between the amount of the product that forms and that product's saturation concentration. Attempts have been made to account for the dependence of saturation vapor pressure on temperature through the Clausius-Clapeyron equation and an estimated heat of vaporization that must be determined experimentally [*Strader et al.*, 1999].

2.4. Absorptive Partitioning

[9] Recent theoretical derivations and experimental studies have shown that the formation of organic aerosol under dry conditions is best described by a dynamic equilibrium for species that exist in both the gas-and aerosol phases [*Pankow*, 1994a, 1994b; *Odum et al.*, 1996, 1997; *Hoffmann et al.*, 1997; *Griffin et al.*, 1999; *Pankow et al.*, 2001]. This equilibrium is based on absorptive (incorporation into the bulk) as opposed to adsorptive (adhesion to the aerosol surface) partitioning [*Liang et al.*, 1997]. It can be described by a partitioning coefficient that depends on temperature, the average molecular weight of the absorbing aerosol, the activity coefficient of the partitioning species in the condensed phase, and the vapor pressure of the species. Calculation of partitioning coefficients requires knowledge of the chemical identities and properties of all species in the condensed phase. Because of the equilibrium established between the gas and particle phases, species can partition to the absorbing organic phase at concentrations below their individual saturation vapor pressures. The partitioning of an SOA also constituent is enhanced by the presence of additional POA or SOA species [*Pankow*, 1994a, 1994b].

[10] Smog chamber studies have extended the theory of *Pankow* [1994a, 1994b] and linked it to the SOA yield [*Odum et al.*, 1996, 1997; *Hoffmann et al.*, 1997; *Griffin et al.*, 1999]. In such studies, multiple products are formed in constant stoichiometric yield from the oxidation of a parent organic and then partition between an absorptive organic

aerosol phase and the gas phase. Analysis of a series of experiments with a given parent allow for the estimation of average stoichiometric factors and partitioning coefficients for the resulting product mix. It has been shown that two surrogate products (described by two mass-based stoichiometric parameters and two equilibrium partitioning coefficients) adequately represent observed aerosol formation from the complex mixture of products resulting from oxidation of a given parent organic [*Odum et al.*, 1996]. While this technique avoids the necessity of chemical identification and characterization, a limitation of this technique is that these parameters are derived using smog chamber experimental data, which may not be robustly extended to the atmosphere. Smog chamber concentrations usually exceed ambient concentrations, and only minimal information regarding the effects of increased humidity and variable temperature are available [*Cocker et al.*, 2001].

2.5. Henry's Law

[11] One approach used to approximate the formation of SOA in models describing regional air quality is to assume that the secondary organic compounds associated with PM are absorbed into only the aqueous phase. This absorption is governed by Henry's law [*Jacobson*, 1997; *Aumont et al.*, 2000], and activity coefficients of organic solutes are typically assumed to be unity. In this manner, only water-soluble organic species are taken into account; those that partition via condensation (absorption into an organic medium or adsorption to aerosol surfaces) are ignored. Once the liquid water content (LWC) of an existing aerosol is assumed or calculated, the amount of OA present in the particle phase is calculated using Henry's law. If the Henry's law coefficient has not been measured, it is assumed that it can be derived using a group contribution method if the structure of the organic compound of interest is known [*Hine and Mookerjee*, 1975; *Suzuki et al.*, 1992]. In addition to considering only those organics that are water-soluble, a limitation associated with this technique is that Henry's law, without activity correction, applies only for solutions that are dilute, which is generally an irrelevant condition for ambient aerosols.

3. Partitioning Model

[12] The purpose of this work is to develop a thermodynamic model for the phase and composition distribution of both inorganic and organic aerosol constituents. A major feature of the model is the distinction between those organic oxidation products that are considered hydrophilic (water-soluble organic compounds, WSOC) and those that are considered hydrophobic. This is done for three reasons: to simplify the set of equations that need to be solved simultaneously (thereby reducing computational demand), to avoid unrealistically high activity coefficients that would result if hydrophobic and hydrophilic species were forced to reside in the same condensed phase, and to more accurately account for dissociation of acidic hydrophilic compounds. Speciation of the hydrophobic and hydrophilic compounds is required for application of the current methodology; an example of the speciation of organic oxidation products will be described in section 4. Because of the large number of atmospheric organic compounds that fall into each of these categories, for application to three-dimensional atmospheric models it is necessary to choose surrogate compounds to represent each group. These surrogates will also be described in section 4, which describes implementation of the SOA module into three-dimensional models.

[13] In the following module description, the following definitions will be used. POA species are emitted directly to the atmosphere and are considered completely nonvolatile. Such species act as partitioning media for hydrophobic SOA species and have no associated particulate water. SOA species are formed only by gas-phase oxidation of volatile organic compounds and are described here as being semivolatile. There is, of course, the possibility that primary semivolatile species are emitted in both the particle and gas phases. When the module described here is incorporated into a three-dimensional atmospheric model, the emitted particulate mass of such species is treated as nonvolatile POA. The mass of such species in the gas phase is treated as a VOC that may form hydrophobic or hydrophilic SOA species via gas-phase oxidation and is lumped into parent groups as discussed in part 1 [*Griffin et al.*, 2002].

[14] SOA species can be further subdivided (hydrophobic or hydrophilic) based on the predominant partitioning mechanism. Hydrophobic SOA constituents partition via absorption into an organic phase consisting of POA and other SOA species (condensation due to low volatility). Hydrophilic OA constituents interact with inorganic aerosol constituents such as nitrate, sulfate, ammonium, etc.; therefore, the module that has been developed to predict dissolution of WSOC is used in conjunction with an inorganic gas-aerosol equilibrium model such as SCAPE2 [*Kim et al.*, 1993; *Meng et al.*, 1995] or ISORROPIA [*Nenes et al.*, 1998], which predict the equilibrium distribution of inorganic aerosol constituents and the corresponding aerosol LWC and pH. Just as molecular and ion solutes are treated in SCAPE2 or ISORROPIA, the hydrophilic group of organic compounds is divided into two subgroups: electrolytes and molecular solutes. However, because data describing the equilibrium in mixed inorganic/organic/aqueous systems largely do not exist [*Macedo et al.*, 1990; *Kicic et al.*, 1991; *Clegg et al.*, 2001], the inorganic and organic fractions are, at present, treated separately, coupled only through the LWC and pH of the aerosol. At this time, due to the lack of this information, this is deemed the most appropriate approach for the development of a first-generation SOA module. When data on such inorganic/organic/aqueous systems become available, the SOA module will be appropriately updated. Figure 1 shows the categorization of ambient constituents, inorganic and organic, modeled in the entire aerosol module.

3.1. Hydrophobic Module

[15] The partitioning of compound i between the gas and particle phases can be described by defining a partitioning coefficient, K_i (m^3 μg^{-1}) [*Pankow*, 1994a, 1994b],

$$K_i = \frac{A_i/\mathrm{TSP}}{G_i}, \tag{1}$$

where A_i (μg m^{-3} air) is the concentration of the compound in the aerosol phase, G_i (μg m^{-3} air) is the concentration of the compound in the gas phase, and TSP (μg m^{-3} air) is the concentration of total suspended PM. This partitioning coefficient describes the equilibrium phase distribution of compound i when both adsorptive and absorptive partition-

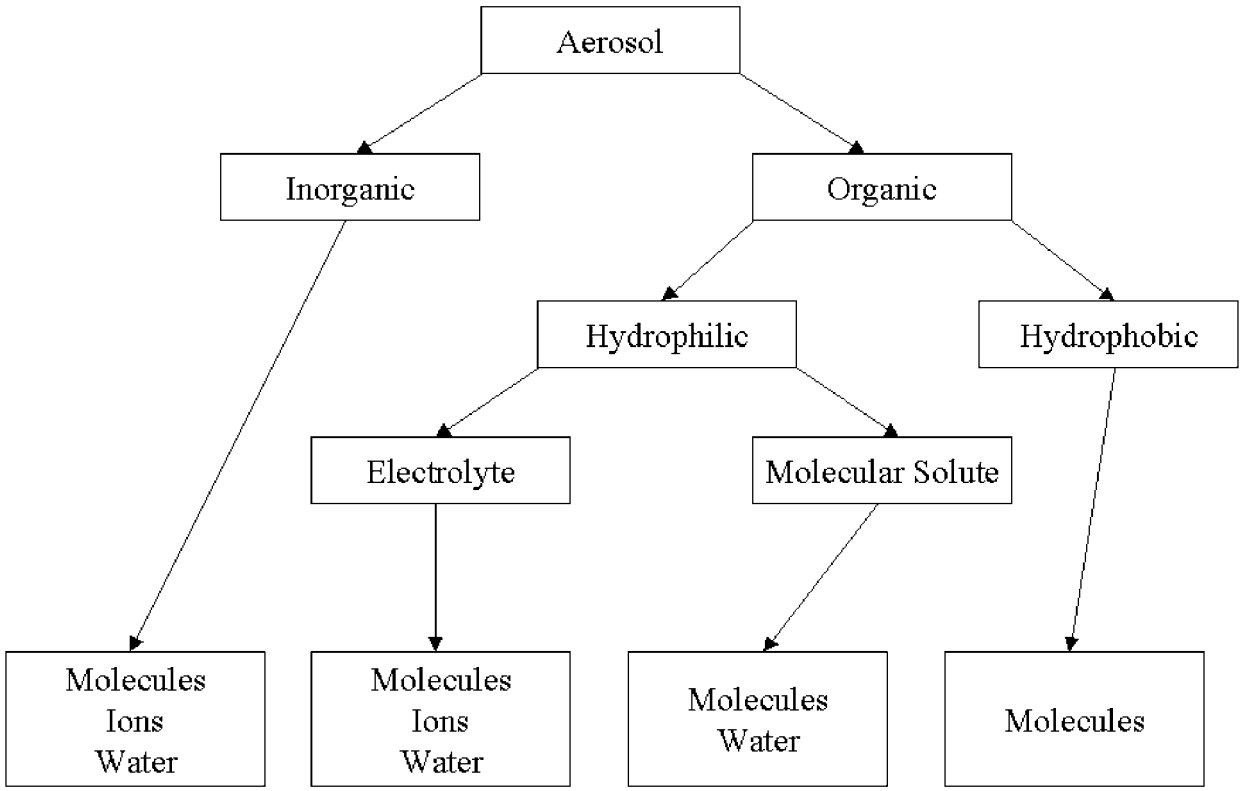

Figure 1. Module categorization of aerosol constituents based on their atomic nature (inorganic versus organic), water affinity (hydrophobic versus hydrophilic), and dissociative properties (electrolytic versus molecular).

ing occur. As stated previously, it has been demonstrated that absorption is the dominant mode of partitioning for organic species in the urban environment [*Liang et al.*, 1997]. To derive an expression for an equilibrium coefficient for absorptive partitioning, only that aerosol mass that is part of an absorptive organic mixture is taken into account,

$$K_{i,om} = \frac{A_{i,om}/M_o}{G_i}, \qquad (2)$$

where the subscript *om* represents the absorbing organic phase, and M_o (μg m^{-3} air) is the total concentration of the absorptive material (both POA and SOA) in the *om* phase. M_o is assumed to be equal to the product of f_{om} and TSP, where f_{om} is the absorptive organic fraction of the PM. Because POA species have no associated water and the SOA species that partition to POA are hydrophobic, M_o does not include water in the work discussed here.

[16] To develop a thermodynamic expression for $K_{i,om}$, the concentration variables in equation (2) are converted to molar units, the ideal gas law is applied, Raoult's Law is invoked, and the definition of mole fraction is incorporated. A more detailed derivation is given by *Pankow* [1994a, 1994b]. The resulting expression is

$$K_{i,om} = \frac{760RT}{10^6 \overline{M}_{om} \gamma_i p^o_{L,i}} = \frac{A_{i,om}/f_{om}\mathrm{TSP}}{G_i} = f(T, x_i), \qquad (3)$$

where R is the ideal gas constant (0.82 m^3 atm mol^{-1} K^{-1}), T (K) is the absolute temperature, $\overline{M}_{om}$ is the average molecular weight (g mol^{-1}) of the *om* phase, γ_i is the activity coefficient of species *i* in the *om* phase (pure solvent reference state), and $p^o_{L,i}$ (torr) is its subcooled liquid vapor pressure at the temperature of interest.

[17] It is seen in equation (3) that the absorptive partitioning of a compound between an *om* phase and the gas phase is strictly a function of temperature (explicitly and implicitly through vapor pressure) and the composition (through both the average molecular weight and the activity coefficient) of the *om* phase. Assuming that vapor pressures are known or can be estimated for a given temperature [*Myrdal and Yalkowsky*, 1997] and that activity coefficients can be estimated, for example, by a group contribution method such as UNIFAC [*Fredenslund et al.*, 1977; *Pankow et al.*, 2001], it is possible to predict the fraction of each compound (i = 1 to n, where n is the number of condensable compounds) that resides in each phase. This is done by solving iteratively a set of implicit simultaneous equations that includes equation (2), equation (3), a mass balance for each compound (the set total concentration of compound i is equal to the sum of its gas-and particle phase concentrations), and the fact that the sum of $A_{i,om}$ values plus all POA concentrations must equal M_o. These constraints make modeling SOA formation via thermodynamic principles feasible as the number of equations reduces to n, with n unknowns (each $A_{i,om}$).

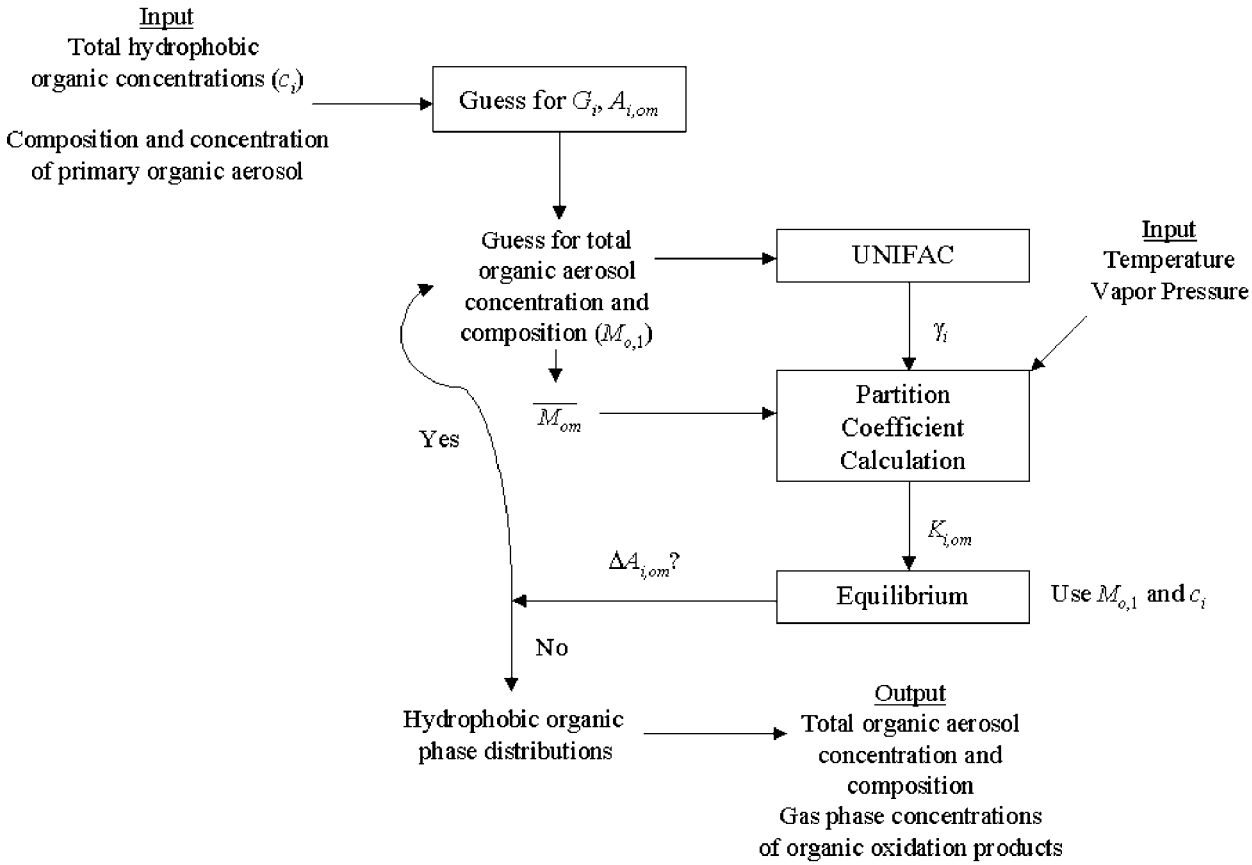

Figure 2. Calculation of the partitioning of hydrophobic SOA constituents between the gas and aerosol phases. Steps include an initial guess for the aerosol phase concentrations ($A_{i,om}$), calculation of the average molecular weight of the aerosol phase, use of UNIFAC to determine activity coefficients (for both SOA and POA species), calculation of theoretical partitioning coefficients for each SOA species, and iteration on the vector of $A_{i,om}$ values.

[18] The hydrophobic module is shown schematically in Figure 2. Required inputs include the concentration and composition of any nonvolatile POA and the total concentrations of the secondary hydrophobic OA constituents. Again, POA species are considered nonvolatile, meaning that they reside completely in the particle phase. (In three-dimensional applications it is assumed that a compound does not partition to the gas phase if it is emitted in the particle phase.) POA species, however, do play a key role in this module by contributing to M_o and $\overline{M}_{om}$ and by affecting activity coefficients. (POA species are included in the UNIFAC calculations.)

[19] An initial distribution of the hydrophobic organics is assumed, to obtain a first approximation for the mass concentration (denoted $M_{o,1}$ in Figure 2) and composition of the absorbing OA, including POA species. The initial guess for the distribution is determined based on the volatility of the semivolatile product being absorbed. From this composition, the average molecular weight of the absorbing phase can be calculated. This composition is also used in UNIFAC to calculate the activity coefficients of the POA and the partitioning hydrophobic species. With temperature and a vapor pressure (experimentally determined or estimated using a group contribution method such as that of *Myrdal and Yalkowsky* [1997]) defined, the next step is to calculate an absorptive partitioning coefficient as in equation (3) for each condensing species. Using these partitioning coefficients with $M_{o,1}$ and each individual total concentration (c_i in Figure 2), it is possible to calculate a new guess for each G_i based on this equilibrium (from equation (2)). A new $A_{i,om}$ value for each species is then found from a mass balance (c_i, the new guess for G_i). These $A_{i,om}$ values are compared to the initial guesses, and the n $A_{i,om}$ values become the iterated variables. Once the series of $A_{i,om}$ values no longer changes by more than a prescribed small value, the calculations of the hydrophobic module are complete. In these calculations, it is also ensured that the gas-phase concentrations of all compounds do not exceed their saturation vapor pressures.

3.2. Hydrophilic Module

[20] Partitioning of WSOC between the gas and aqueous phases is governed by

$$H^{HL}i = \frac{c_{w,i}}{p_i} = \frac{A_i \gamma^{HL_i}}{M_i(\mathrm{LWC})p_i}, \quad (4)$$

where $H^{HL}i$ (μM atm^{-1}) is the Henry's law constant of species i, determined, for example, by a group contribution

method, $c_{w,i}$ is its aqueous phase concentration (μmol l^{-1} of water), and p_i (atm) is the gas phase partial pressure of species i. Here, A_i ($\mu g\ m^{-3}$) still represents the aerosol phase concentration of i, but in this case it refers to the aqueous phase. M_i is the molecular weight of the compound (g mol^{-1}), and γ^{HL_i} is its activity coefficient in the aqueous mixture (infinite dilution reference state). LWC in this case has units of l of water per m^3 of air. The second half of this expression is a simple unit conversion from the conventional definition of a Henry's law constant [*Schwarzenbach et al.*, 1993]. For organic acids, solubility is enhanced by the dissociation of molecular solutes into ions, which is governed by equilibrium acid dissociation constants,

$$K_{a,i} = \{H^+\}\{\mathrm{ORG-Anion}_i\}/\{\mathrm{ORG}_i\}, \quad (5)$$

where $K_{a,i}$ is the acid dissociation constant of organic species i (ORG_i) and the bracketed notation represents the activities of the species of interest. ORG-$Anion_i$ represents the dissociation product. Acid dissociation constants can also be estimated by structure-activity relationships [*Harris and Hayes*, 1982; *Schwarzenbach et al.*, 1993].

[21] As shown in equation (4), the partitioning of WSOC depends on the activity coefficient of the species in the aqueous mixture. Such activity coefficients measure the deviation from ideality, which is usually significant for highly concentrated ambient aerosols. Various methods can be used to calculate the activity coefficients of ions (see *Kim et al.* [1993] for more detail), each of which considers only inorganic ion-ion interactions. Limited data for inorganic-organic ion-ion interactions are available [*Clegg et al.*, 2001]. For molecular solutes, UNIFAC can be used to estimate activity coefficients. While UNIFAC was not designed for use with highly polar compounds such as those that are constituents of SOA, it is assumed here that the UNIFAC group contribution parameters for functionalities such as COOH, CHO, CH_2, etc., can be applied to the surrogate molecules. Some parameters are available to treat the interactions between molecular groups and inorganic ions within the UNIFAC framework [e.g., *Kicic et al.*, 1991; *Yan et al.*, 1999]. Unfortunately, key inorganic components in the atmosphere, such as ammonium and sulfate, are not included in these studies.

[22] Ideally, the aerosol system would be treated as an interacting mixture of inorganics, organics, and water [*Clegg et al.*, 2001]. Because of the lack of experimental data, however, traditional methods of estimating activity coefficients cannot be used for interactions between inorganic and organic ions. Therefore, a number of assumptions must be made. Most importantly, it is assumed that inorganic and organic solutes do not interact. This allows for the decoupling of the organic partitioning of WSOC from the inorganic model (e.g., SCAPE2), in terms of calculating activity coefficients. Also as a result of this assumption, the formation of organic-inorganic salts is not represented. Second, it is assumed that the activity coefficients of the organic ions are equivalent to those of the corresponding molecular solute. An alternative formulation may be to assume that the proton activity coefficient is controlled by the inorganic solutes and calculate the activity coefficient of the anion based on the ion pair approach. Assumptions about the activity coefficients impact substantially the modeling results because the values of these variables span orders of magnitude. Although these assumptions need to be evaluated when experimental data become available, they are deemed appropriate for the development of a first-generation inorganic/organic model.

[23] The LWC of the aerosol is also a key parameter in determining the Henry's law partitioning of WSOC. Because of its simplicity, the Zdanovskii-Stokes-Robinson (ZSR) method is used in three-dimensional atmospheric models to determine the water content of the aerosol solution [see, e.g., *Meng et al.*, 1998]. The basic assumption of the ZSR method is that the quantities of water associated with each solute are additive. Therefore, LWC (here, μg water m^{-3} air) is defined by

$$\mathrm{LWC} = \sum_i \frac{m_i}{m_{i0}(a_w)}, \quad (6)$$

where m_i is the molar concentration of species i (mol i m^{-3} of air) and $m_{i0}(a_w)$ is the molality of species i (mol i μg^{-1} water) in a binary mixture at the water activity of interest (a_w). Although polynomial fits for inorganic solute concentrations as a function of water activity have been developed by *Kim et al.* [1993] and *Meng et al.* [1995] based on experimental data, this approach is not possible for organic solutes due to lack of activity measurements. An estimation method must be used to determine water activities for binary or multicomponent organic systems. In this regard, UNIFAC can be used to determine the molality of organic solutions at specific water activity, which is equal to the relative humidity at equilibrium [*Saxena and Hildemann*, 1996]. The water associated with the inorganic and organic components is then considered and used in equation (6) to determine the LWC of the aerosol of interest.

[24] The hydrophilic module is shown schematically in Figure 3. The required inputs for the hydrophilic module include the SCAPE2 output (LWC and the concentration of hydrogen ions) and the total concentrations of the partitioning secondary hydrophilic organics. The first step in the hydrophilic module is to determine the type of calculation that must be performed. If there is no existing aqueous phase, a calculation using both hydrophilic and hydrophobic species in the hydrophobic module (termed here a saturation calculation) is performed. This is because there is no LWC into which hydrophilic SOA compounds can partition; dissociation cannot be taken into account in this case. This situation is highly unlikely to occur in the ambient air. Subsequent to this saturation calculation, if the relative humidity (RH) is below the deliquescence relative humidity (DRH) of all WSOC species present [*Saxena and Hildemann*, 1997], the organic phase remains dry. Conversely, if RH is greater than the DRH of any of the hydrophilic species, a new aqueous phase is formed. When a new aqueous phase is formed, the inorganic aerosol remains unaffected since experimental data indicate that the presence of organics does not change the DRH of inorganic aerosol [*Cruz and Pandis*, 2000].

[25] If an aqueous phase does exist at the start of the hydrophilic module calculation, a saturation calculation is performed only if RH is less than the DRH of all of the hydrophilic organic species. In such a case, the hydrophilic

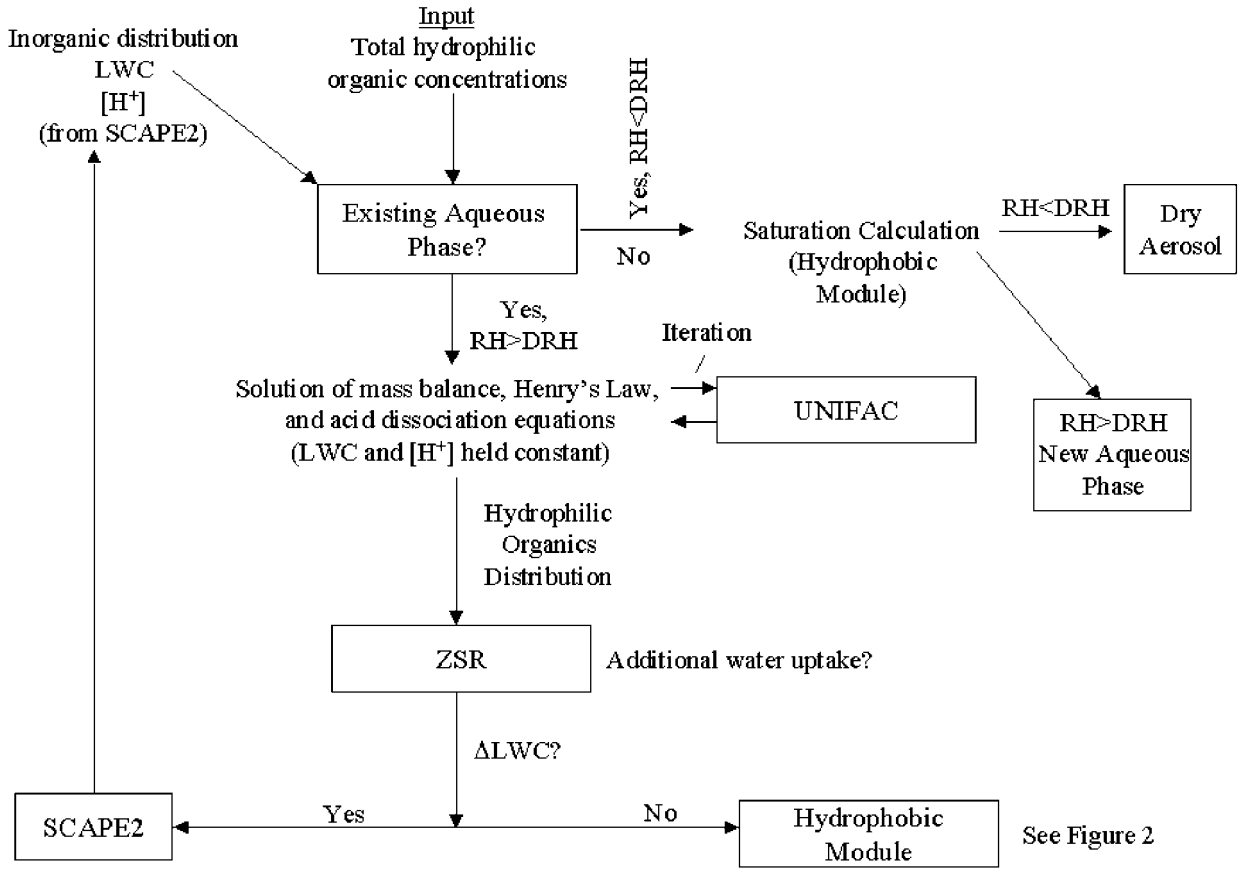

Figure 3. Calculation of the partitioning of hydrophilic SOA constituents between the gas and aqueous phases. Steps include determination of the type of calculation to be performed (saturation versus aqueous equilibrium), iterative solution of mass balance, Henry's law, acid dissociation constant equations (including iteration in UNIFAC to determine activity coefficients), calculation of water uptake associated with aqueous organics, and iteration on LWC between the hydrophilic module and an inorganic module such as SCAPE2.

SOA compounds will not partition to the aqueous phase. This is again highly unlikely in the ambient air. Otherwise, if RH is greater than the DRH of any species, an aqueous equilibrium calculation is performed. The equilibrium calculation involves simultaneously solving mass balance (total concentration, c_i, is equal to the sum of the concentrations in the gas and aqueous phases), Henry's law (equation (4)), and acid dissociation equations for each species (both ions and molecules) (equation (5)).

[26] Iteration (using a Newton line search method) is required because the activity coefficients are a strong function of the aerosol composition. Once equilibrium values based on the input LWC are reached, an organic-water system is considered to calculate the additional amount of water that is taken up as a result of the presence of the hydrophilic organics. (Recall that RH is greater than at least one DRH in this scenario.) If the change in LWC is significant, the new total LWC and the concentrations of organic ions are passed to SCAPE2 to determine if the distribution of the inorganic aerosol constituents is affected. If this change in LWC is insignificant, the output from the hydrophilic module includes the phase distribution of inorganic aerosol constituents, the phase distribution of hydrophilic organic aerosol constituents, and the LWC of the aerosol. In this regard, LWC is used as an iterative variable that must be consistent between the inorganic and hydrophilic modules.

[27] Similar to the work presented by *Seinfeld et al.* [2001], the hydrophilic module described here will predict an increase in SOA formation as a result of an increase in the LWC of the aerosol through an increase in RH. This is due to the affinity for water exhibited by each of the compounds classified as hydrophilic. There is no interaction between the hydrophobic and hydrophilic fractions of the organic aerosol. Therefore, the partitioning of hydrophobic SOA constituents is not affected by RH as described by *Pankow et al.* [1993]. However, in that study, in contrast to the present one, the authors were investigating the partitioning only of hydrophobic, nonpolar compounds.

3.3. Case Studies

3.3.1. Hydrophobic Module

[28] In order to demonstrate the hydrophobic portion of the model, we define a surrogate SOA compound and a prescribed mixture of POA constituents. These POA species

Table 1. Assumed POA Composition for Evaluation of the Hydrophobic Module

	Fatty Acids	Substituted Phenols	Alkanes	Aromatic Acids
Mass fraction	0.57	0.11	0.17	0.15
Surrogate structure	tetracosanoic acid (C_{24} *n*-acid)	acetonyl syringol (2,6-dimethoxy-4-acetonyl-phenol)	nonacosane (C_{29} *n*-alkane)	phthalic acid (1,2-benzene-dicarboxylic acid)

are used only for the evaluation of the hydrophobic module and are only used for illustrative purposes. They will not be used when the SOA module is incorporated into three-dimensional atmospheric models, as described in section 4.

[29] Representative POA constituents have been reported, for example, based on measurements made in the Los Angeles Basin [*Rogge et al.*, 1993] and the San Joaquin Valley of California [*Schauer and Cass*, 1998]. Major classes of organic compounds resolved in the analysis of OA include fatty acids, substituted phenols, aromatic acids, alkanes, and, for the San Joaquin Valley, levoglucosan and other sugar derivatives. Surrogate POA constituents, excluding those that were shown to have affinity toward the aqueous phase, are chosen from this group based on their observed predominance in the ambient samples described above (Table 1). Octadecanoic acid is selected as the surrogate hydrophobic SOA constituent.

[30] The first variable investigated in the evaluation of the hydrophobic module is TSP (with initial f_{om} set to 0.1 for this study in order to match the value used by *Pankow* [1994a, 1994b]). For a fixed total amount of octadecanoic acid present (1 $\mu g\ m^{-3}$), increasing initial TSP (from 10 to 100 $\mu g\ m^{-3}$) and, therefore, the mass of each POA constituent (TSP $\times$ 0.1 $\times$ mass fraction given in Table 1), results in an increase in the amount of octadecanoic acid that partitions to the aerosol phase (A) from approximately 0.35 to 0.8 $\mu g\ m^{-3}$ (Figure 4). The resulting changes in average molecular weight and activity coefficients lead to a small decrease in the partitioning coefficient (K) of octadecanoic acid.

[31] Partitioning can also be investigated when the total concentration of octadecanoic acid varies at total fixed TSP (50 $\mu g\ m^{-3}$, yielding 5 $\mu g\ m^{-3}$ of POA with mass fractions defined by Table 1). Naturally, increasing the concentration of octadecanoic acid leads to an increase in its amount partitioning to the aerosol phase (A) (Figure 5). Changes in the average molecular weight of the absorbing medium and the activity coefficients lead to modest increases in the partitioning coefficient (K) as the total acid concentration is increased.

3.3.2. Hydrophilic Module

[32] In order to demonstrate the hydrophilic module, malic (COOH-CH_2-CHOH-COOH) and glyoxalic (CHO-COOH) acids are chosen as surrogate WSOC. The properties of these compounds are given in Table 2. Malic acid is very soluble; glyoxalic acid is only sparingly so. Table 3 shows the input conditions and predictions from the hydrophilic module when acting independent of any inorganic module. Because of its high solubility, virtually all of the malic acid partitions to the aqueous phase, with the ions being the dominant forms. Glyoxalic acid, on the other hand, tends to remain in the gas phase. For what little amount partitions to the aqueous phase, the ion is again the dominant form. The ionic form is prevalent because of the relatively high pH value used in this illustrative example. A

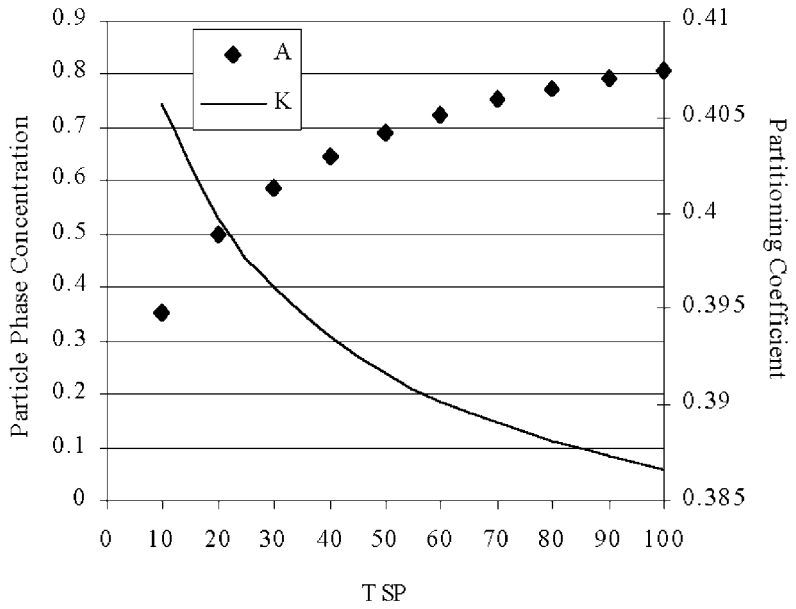

Figure 4. Particulate concentrations (A) of octadecanoic acid ($\mu g\ m^{-3}$) and its partitioning coefficient (K) ($m^3\ \mu g^{-1}$) as a function of TSP. TSP is assumed to have an initial organic mass fraction of 0.1, with the speciation of the organic phase described in Table 1. Total concentration of octadecanoic acid = 1 $\mu g\ m^{-3}$.

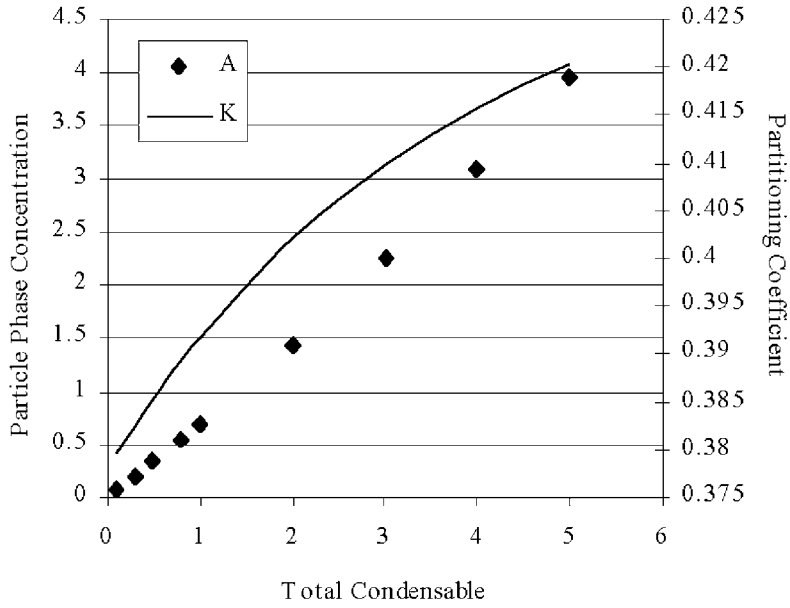

Figure 5. Particulate concentrations (A) of octadecanoic acid ($\mu g\ m^{-3}$) and its partitioning coefficient (K) ($m^3\ \mu g^{-1}$) as a function of the total amount of octadecanoic acid (condensable) present. TSP = 50 $\mu g\ m^{-3}$ with 10% being organic material speciated according to Table 1.

change in LWC (ΔLWC) of 0.46 ng m^{-3} is observed due to the aqueous phase concentrations of the two acids and their ions.

[33] If other initial conditions are held constant, the ΔLWC that results due to the dissolution of hydrophilic organics increases as RH increases (Figure 6). This is especially important for malic acid, which exhibits deliquescence behavior at approximately 79% RH. Below this humidity, no additional water is associated with the organic aerosol because of the presence of malic acid. Because malic acid is much more soluble, the amount of water associated with malic acid is much greater than that associated with glyoxalic acid, even though both compounds are present at the same total concentrations (gas and aerosol phase combined).

[34] If other initial conditions are again held constant, sensitivity studies also show the overall importance of the aerosol pH (Figure 7). A lower aerosol pH affects the dissociation of acids, resulting in molecular solutes being favored over the ionized forms. An increased pH results in a higher effective Henry's law constant for the acids, yielding higher organic concentrations. This increase in the organic concentration also leads to an increase in ΔLWC. These effects are especially evident for glyoxalic acid. Because of the high solubility of malic acid, pH has little effect on the amount of water associated with this species.

[35] The hydrophilic organic module was also evaluated in conjunction with SCAPE2, using both inorganic and WSOC constituents (Table 4). In this example, only limited inorganic species are present (ammonia and nitric acid) so that the interactions between inorganics and hydrophilic organics (malic and glyoxalic acids in this case) can be exhibited simply. There are two main effects of the organic solutes. First, the extra water associated with the WSOC induces additional partitioning of the inorganics to the aqueous phase. Second, the decrease in pH favors the

Table 2. Properties of Malic and Glyoxalic Acids

	Malic Acid	Glyoxalic Acid
H_i[a]	2×10^{13} M atm^{-1}	9×10^3 M atm^{-1}
K_a[b]	3.98×10^{-4} M	6.61×10^{-4} M
Ka_2[b]	7.76×10^{-6} M	–

[a] Henry's law coefficient, *Saxena and Hildemann* [1996].
[b] Acid dissociation constants, *Lide* [1997]. K_{a2} represents dissociation of the second acid group of malic acid.

Table 3. Input and Output for the Evaluation of the Hydrophilic Module[a]

	Input
T	298 K
RH	0.8
LWC	1 $\mu g\ m^{-3}$
pH	5
MA (t)	1 ng m^{-3}
GA (t)	1 ng m^{-3}
	Output
MA (g)	2.88×10^{-8} $\mu g\ m^{-3}$
MA (aq)	5.88×10^{-6} $\mu g\ m^{-3}$
MA^-(aq)	5.56×10^{-4} $\mu g\ m^{-3}$
MA^{2-}(aq)	4.28×10^{-4} $\mu g\ m^{-3}$
GA (g)	1.00×10^{-3} $\mu g\ m^{-3}$
GA (aq)	1.24×10^{-10} $\mu g\ m^{-3}$
GA^-(aq)	1.48×10^{-8} $\mu g\ m^{-3}$
ΔLWC	0.46 ng m^{-3}

[a] MA, malic acid; GA, glyoxalic acid; (t), total available material; (g), gas-phase concentration; (aq), aqueous-phase concentration; ORG^-, first dissociation product; ORG^{2-}, second dissociation product; ΔLWC, change in LWC due to the presence of the aqueous organics.

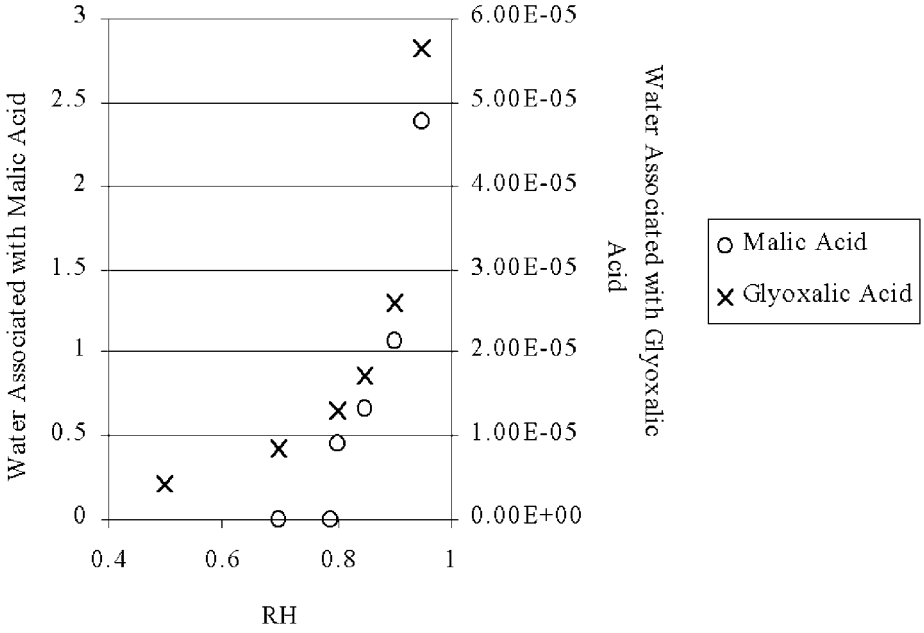

Figure 6. Sensitivity of the water associated with malic and glyoxalic acids (ng m^{-3}) to varying RH in the hydrophilic module. Other initial conditions: LWC = 1 μg m^{-3}, pH = 5, and total of each solute = 1 ng m^{-3}.

dissolution of basic gases (e.g., ammonia) as opposed to acidic gases (e.g., nitric acid). For example, in the case shown in Table 4, the final concentration of NH_4^+ is 0.078 μmol m^{-3}, while in the absence of organics, the concentration of NH_4^+ would be 0.064 μmol m^{-3}.

[36] In each of the modules and in all of the cases tested, the typical number of iterations required was less than 10. While this number depends on the total concentrations of the partitioning compounds, even the most difficult cases converged in less than 20 iterations. The iterative calculations of

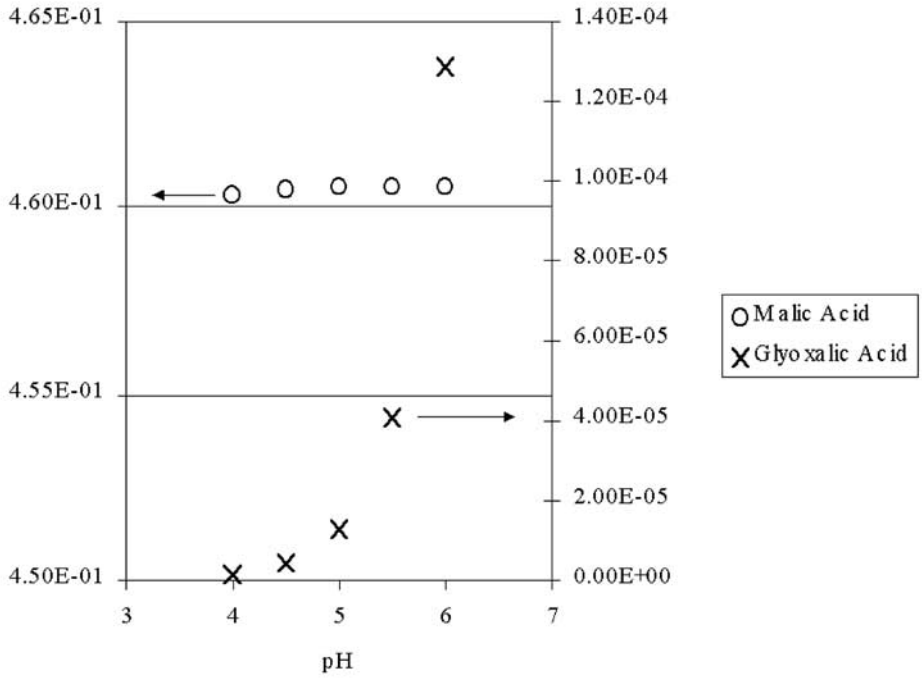

Figure 7. Sensitivity of the water associated with malic and glyoxalic acids (ng m^{-3}) to varying pH in the hydrophilic module. Other initial conditions: LWC = 1 μg m^{-3}, RH = 0.8, and total of each solute = 1 ng m^{-3}.

Table 4. Input and Output for the Evaluation of the Hydrophilic Module Used in Conjunction With SCAPE2

Component	Value
Input to SCAPE2	
Total NH_3	0.1 μmol m^{-3}
Total HNO_3	0.1 μmol m^{-3}
Temperature	298 K
Relative humidity	0.8
Output of SCAPE2 (Initial Input to Hydrophilic Module)	
LWC (inorganic)[a]	15.4 μg m^{-3}
pH	2.28
Additional Input to Hydrophilic Module	
Total glyoxalic acid	0.1 μmol m^{-3}
Total malic acid	0.1 μmol m^{-3}
Output of First Pass of Hydrophilic Module	
LWC (organic)[a]	14.4 μg m^{-3}
Total organic ions (aq)	0.0071 μmol m^{-3}
Total organic molecules (aq)	0.0928 μmol m^{-3}
LWC (total)[a]	29.8 μg m^{-3}
Output of SCAPE2 and Hydrophilic Module After Iteration on Total LWC	
LWC (inorganic)[a]	17.5 μg m^{-3}
pH	2.15
LWC (organic)[a]	14.4 μg m^{-3}
Total organic ions (aq)	0.0053 μmol m^{-3}
Total organic molecules (aq)	0.0947 μmol m^{-3}
LWC (total)[a]	31.9 μg m^{-3}

[a] LWC (inorganic), water associated with inorganics; conversely, LWC (organic), water associated with organics; LWC (total), sum of the two; (aq), aqueous phase concentrations.

activity in the aqueous phase are typically the most computationally demanding.

4. Implementation in Atmospheric Models

[37] The integration of the aerosol module in an atmospheric model is depicted in Figure 8. Figure 8 only describes module implementation needs for three-dimensional atmospheric models; part 3 of this series of papers addresses module application. The first set of inputs includes total inorganic concentrations, relative humidity, and temperature. Computationally, this information is passed to the inorganic thermodynamic equilibrium module, the output from which includes the phase and composition distribution of the inorganics and the LWC and pH of the inorganic/water aerosol. If the LWC of the aerosol is zero at this point, a hydrophobic calculation is performed considering all (both hydrophobic and hydrophilic) semivolatile organic oxidation products. At this point, water uptake of the hydrophilic products only is considered, and the aerosol calculations for the current time step are complete. On the other hand, if the LWC is nonzero after the inorganic calculations (which is the realistic atmospheric condition), its value and that of the pH are passed to the hydrophilic module, along with total concentrations of the hydrophilic organic oxidation products. After these products have been partitioned computationally and the water taken up as a result has been calculated, the total LWC is passed back to inorganic aerosol model to determine if the additional water and the presence of organic ions affect the distribution of the inorganic species. Once the LWC is internally consistent between the inorganic and the hydrophilic organic calculations, the hydrophobic module, which requires total concentrations of the POA constituents and the hydrophobic organic oxidation products, is called. Once the hydrophobic module (which is the last step of the aerosol calculations) determines the appropriate equilibrium distribution for the participating products, predictions include the LWC and the concentrations of all organic oxidation products and inorganic species in each phase.

[38] In its three-dimensional application, the partitioning module is linked to a gas-phase chemical mechanism that predicts the concentrations of semivolatile or nonvolatile organic oxidation products. The Caltech Atmospheric Chemistry Mechanism (CACM) involves over 190 species participating in over 360 reactions [*Griffin et al.*, 2002]. As described in part 1, there are over 40 compounds specified in CACM that are considered capable of forming SOA because of their solubility or low vapor pressures. Predicting the partitioning of that number of species is likely to be too computationally demanding, especially in light of the lack of thermodynamic data for multifunctional organic species to support such a detailed speciation. Therefore, these secondary products are further lumped into one of ten groups. The first separation is made on the basis of affinity for water. An organic is considered water-soluble based on the length of the carbon chain ($\leq$7 carbons), its solubility (solubility $\geq$1 g solute/100 g water), and its effective Henry's law coefficient ($\geq 1\ 10^6$ M atm^{-1}). Additionally, those species with seven or more carbon atoms and three functional groups are considered water-soluble because these compounds exhibit such a high degree of polarity [*Saxena and Hildemann*, 1996]. Compounds meeting these criteria are defined as hydrophilic and can be further subdivided by size (low or high carbon number), source (anthropogenic or biogenic), and dissociative properties (present only as molecular solutes or as both ions and molecules). This process results in five hydrophilic surrogates. The products from CACM that fall into each group are structurally averaged (number of carbon, number and type of functional groups, etc.) to determine the structure of the five surrogates to be used in the hydrophilic module. Five surrogates for the hydrophobic module were determined similarly. The hydrophobic compounds are divided based on source (anthropogenic versus biogenic), structure (aliphatic versus benzene-based versus naphthalene-based for anthropogenic species), and volatility (for benzene-based anthropogenic species). Reduction of the 42 compounds into 10 (the properties for which are determined using group contribution methods) allows for a substantial reduction in the computational demands of the partitioning module. The 10 resulting compounds and some of their characteristics are described in Table 5a. In some cases, the structure of a surrogate was difficult to determine because the averaging technique predicted a fractional number of certain functional groups. This is most important in surrogate B2, in which the aldehyde group could be replaced by either a hydroxy-or a nitro group. Table 6 shows the reduction of the CACM species into the ten SOA surrogates listed in Table 5a.

[39] Unlike the evaluation studies described in section 3.3, where the composition of the POA, the value of f_{om}, and the concentration of TSP are set, use within a three-dimensional model require chemically resolved POA emissions. In studies of the air quality in the SoCAB, for example, it has been determined that the organic fraction of aerosol emissions can

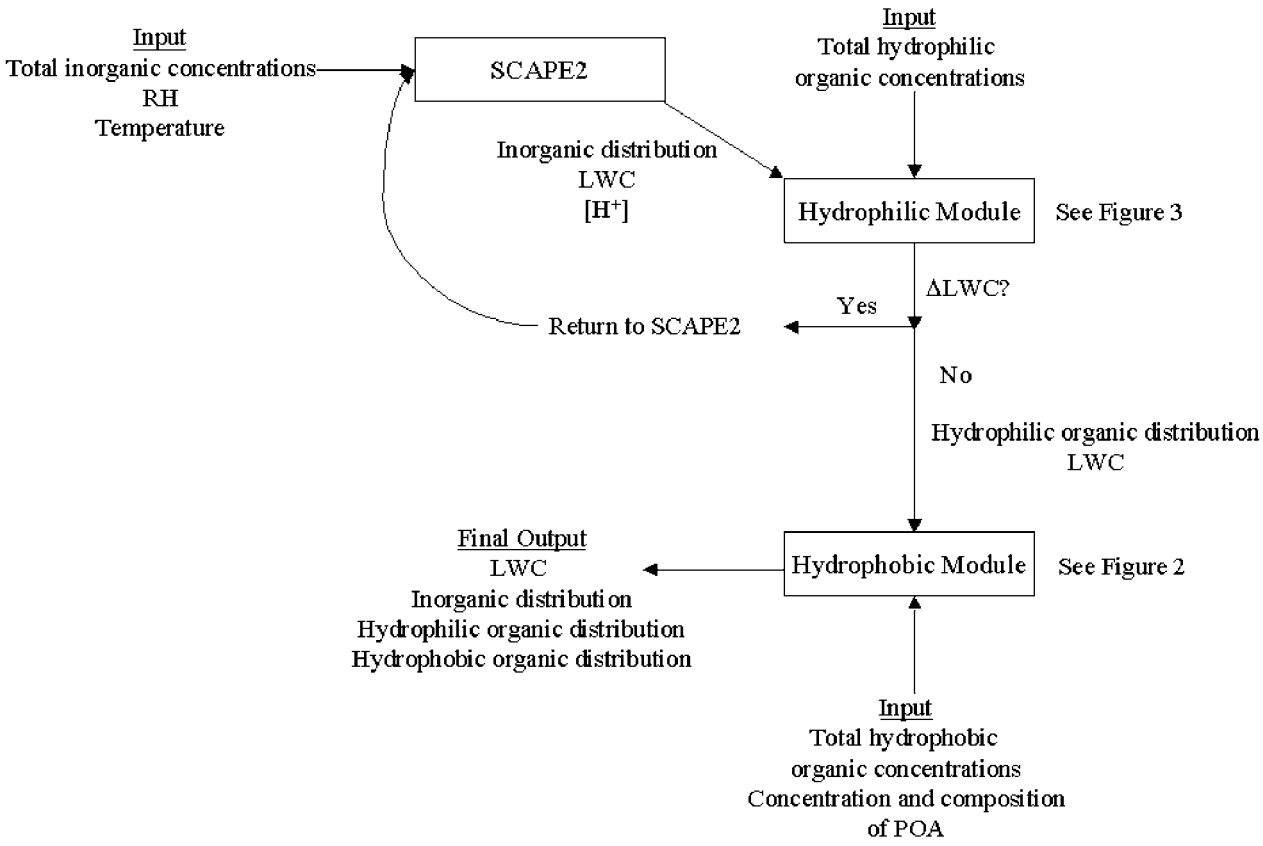

Figure 8. Calculation of aerosol water content and the phase distributions of both inorganic and organic aerosol constituents through use of the described module in a three-dimensional atmospheric model. Steps include the use of SCAPE2 to determine inorganic aerosol LWC and pH, calculations using the hydrophilic module (Figure 3), iteration on LWC with SCAPE2, and calculations using the hydrophobic module (Figure 2).

Table 5a. Surrogate Organic Oxidation Products to be Used in the Partitioning Module in Application in Three-Dimensional Atmospheric Models

Surrogate[a]	Description[b]	#C	COOH	C = O	CHO	OH	ONO_2	NO_2	C = C	$p_{L,i}^{oc}$ (atm)
A1	WSOC, anthropogenic, dissociative, low #C (90)	2	2							7.0E-7
A2	WSOC, anthropogenic, dissociative, high #C (184)	8	2		1				2	1.1E-16
A3	WSOC, anthropogenic, nondissociative (154)	8			2	1			2	1.3E-6
A4	WSOC, biogenic, dissociative (186)	9	1	1		1			1	2.8E-9
A5	WSOC, biogenic, nondissociative (186)	10		1	1	1				1.8E-7
B1	hydrophobic, anthropogenic, benzene-based, low volatility (197)	9	1[d]			1[d]		1[d]		2.4E-9
B2	hydrophobic, anthropogenic, benzene-based, higher volatility (164)	9	1[d]		1[d]					5.5E-8
B3	hydrophobic, anthropogenic, naphthalene-based (181)	12					1			1.0E-7
B4	hydrophobic, anthropogenic, aliphatic (301)	16				1	1			1.8E-8
B5	hydrophobic, biogenic, aliphatic (170)	10		1		1			1	2.2E-6

[a] A, hydrophilic surrogates; B, hydrophobic surrogates.
[b] Number in parentheses representing surrogate molecular weight (g mol^{-1}).
[c] Values at 298 K according to the expressions derived from *Myrdal and Yalkowsky* [1997].
[d] Attached to the aromatic ring as opposed to a side chain alkyl substituent.

Table 5b. Surrogate POA Species to be Used in the Partitioning Module in Application in Three-Dimensional Atmospheric Models

Species	Description	Chemical Name	Description	Molecular Weight, g mol^{-1}
1	*n*-alkanes	*n*-nonacosane	C_{29} *n*-alkane	408
2	polycyclic aromatic hydrocarbons (PAH)	benzo(ghi)-perylene	PAH consisting of five aromatic rings	276
3	oxygenated PAH	2,6-naphthalene-diacid	PAH with two aromatic rings and two acid substituents	216
4	diacids	butanedioic acid	C_4 *n*-diacid	118
5	aliphatic acids	octadecanoic acid	C_{18} *n*-acid	284
6	substituted monoaromatic compounds	phthalic acid	aromatic ring with two acid substituents	166
7	cyclic petroleum biomarkers	17(α)H-21(β)H-hopane	Five fused aliphatic rings with multiple alkyl substituents	412
8	unresolved organics	branched and highly cyclic material	Four fused aliphatic rings with four branched alkyl substituents	390

be classified into eight categories: *n*-alkanes, polycyclic aromatic hydrocarbons (PAH), oxygenated PAH, diacids, aliphatic acids, substituted monoaromatics, cyclic petroleum biomarkers (e.g., hopanes), and unresolved organic matter (characterized by highly cyclic and branched petroleum biomarkers) [*Schauer*, 1998]. For implementation of the SOA module into a three-dimensional model, the predominant species have been identified and their structures are used as surrogates for these classes. POA structures are needed for the hydrophobic module calculations of activity coefficients. Table 5b shows the structure and properties of the eight compounds chosen for the SoCAB.

[40] The final issue that must be addressed in implementing the module discussed here into three-dimensional models

Table 6. Hydrophilic CACM Species Reduction Into Five SOA Surrogates

Surrogate	Characteristics	Surrogate Species[a]	Contributing Species
A1	WSOC, anthropogenic, dissociative, low #C	UR28	UR21: keto-propanoic acid UR28: oxalic acid
A2	WSOC, anthropogenic, dissociative, high #C	RP18	RP13: 2-carboxyl-5-methyl-2,4-hexadiendial RP17: 4-hydroxy-3,5-dimethyl-2,4-hexadienalic acid RP18: 2-methyl-5-formyl-2,4-hexadiendioic acid UR29: 4-hydroxy-3,5-dimethyl-2,4-hexadiendioic acid UR30: 2-methyl-5-carboxy-2,4-hexadiendioic acid
A3	WSOC, anthropogenic, nondissociative	3-hydroxy-2,4-dimethyl-2, 4-hexadiendial	RPR9: 4-hydroxy-3,5-dimethyl-2,4-hexadiendial RP12: 2-methyl-5-formyl-2,4-hexadiendial
A4	WSOC, biogenic, dissociative	2-hydroxy-3-isopropyl-5-keto-3-hexenoic acid	UR3: 2-hydroxy-3-isopropyl-6-keto-heptanoic acid UR23: 3-isopropyl-4-hydroxy-2-butenoic acid
A5	WSOC, biogenic, non-dissociative	RPR3	RPR3: 2-hydroxy-3-isopropyl-6-keto-heptanal AP7: 1-methyl-1-nitrato-2,3-dihydroxy-4-isopropyl-cyclohexane UR17: 2-hydroxy-3-isopropyl-hexadial
B1	hydrophobic, anthropogenic, benzene-based, low volatility	3,5-dimethyl-2-nitro-4-hydroxy-benzoic acid	AP1: 2-nitrooxymethyl-6-methyl-phenol AP6: 4-nitrooxymethyl-benzoic acid UR22: 2,6-dimethyl-3,4-dinitro-phenol UR31: 2-(dimethyl-propenoic acid)-benzoic acid
B2	hydrophobic, anthropogenic, benzene-based, higher volatility	2,4-dimethyl-3-formyl-benzoic acid	ADAC: terephthalic acid RPR4: 2,6-dimethyl-4-nitro-phenol RPR7: 4-formyl-benzoic acid RP14: 2-(dimethyl-propenal)-benzaldehyde RP19: 2-(dimethyl-propenal)-benzoic acid UR2: 3-hydroxy-4-methyl-benzoic acid UR14: 2-nitro-4-methyl-benzoic acid UR27: 2-carboxy-acetophenone
B3	hydrophobic, anthropogenic, naphthalene-based	AP10	AP10: 1-methyl-2-nitrooxymethyl-naphthalene UR11: 1,2-dimethyl-3-hydroxy-naphthalene UR15: 1,2-dimethyl-3-nitro-naphthalene
B4	hydrophobic, anthropogenic, aliphatic	AP12	AP11: 8-hexadecylnitrate AP12: 8-hydroxy-11-hexadecylnitrate UR20: 11-hydroxy-8-hexadecanone UR26: 4,5-Dimethyl-6-keto-2,4-heptadienoic acid UR34: 8-hexadecanone
B5	hydrophobic, biogenic, aliphatic	2-isopropyl-5-methyl-6-hydroxy-2-cyclohexenone	PAN8: peroxy 2-hydroxy-3-isopropyl-6-keto-heptionyl nitrate AP8: 1-methyl-4-nitrato-4-isopropyl-5-hydroxy-cyclohexene UR5: 1-methyl-3-hydroxy-4-isopropyl-1,2-cyclohexane epoxide UR6: 2-hydroxy-3-isopropyl-6-methyl-cyclohexanone UR7: 3,7-dimethyl-6-keto-3-octenal UR8: 3-isopropyl-6-keto-3-heptenoic acid

[a] Detailed description of structural components given in Table 5a. Notation for contributing species is from *Griffin et al.* [2002].

is how the lumping of SOA species for partitioning calculations affects gas-phase reactions. This is important because several of the participating species are reactive in the gas-phase. First, CACM predicts the mixing ratios (ppb) of the species considered capable of contributing to SOA formation. These are then converted to mass concentrations and appropriately summed to give the mass concentration of each surrogate according to the lumping shown in Table 6; at the same time, the mass fraction (χ_i) that each CACM product contributes to its surrogate is calculated. With the total summed mass concentration of each surrogate SOA molecule, the SOA partitioning module is called. Upon completion of this module, gas-phase mass concentrations of each lumped surrogate are available. These concentrations are then multiplied by the appropriate χ_i values to calculate the mass concentrations of each of the CACM species that remain in the gas phase. These individual gas-phase mass concentrations are then converted back to the mixing ratios needed in the gas-phase chemical mechanism. In this way, mass is conserved between CACM and the SOA module.

5. Discussion

[41] Because experimental data on thermodynamic properties of mixed organic-inorganic aqueous solutions are sparse, many necessary assumptions have been made in the development of the partitioning model. First, if an organic species shows affinity for both the aqueous and organic phases, it is chosen as either hydrophobic or hydrophilic, which may result in the underprediction of its amount in the aerosol phase. If appropriate experimental data become available, compounds that display such behavior can be accounted for explicitly. Second, it is assumed that there is no interaction between aqueous phase inorganics and organics. As thermodynamic data become available, such interactions can be incorporated. Third, the ability of certain hydrophobic organic species to limit water uptake has not been taken into account. Any uncertainties associated with UNIFAC and other group contribution methods for estimating thermodynamic properties add to the uncertainty associated with the partitioning module. Despite these limitations, the current module represents the state-of-the-art for describing SOA formation in a three-dimensional atmospheric model.

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